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PHOTO-ELASTIC EFFECT IN CRYSTALS

A New Result for the T_h Class

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1. Introduction

One of us (Bhagavantam, 1942) derived by a group theoretical method the number of independent constants needed to describe the photo-elastic behaviour of each of the 32 crystal classes. It was found that the numbers are at variance with those given by Pockels (1889, 1906) and current in literature, for certain classes, namely, C_4, S_4 and C_{4h} of the tetragonal system C_3, S_6, C_{3h}, C_6, and C_{6h} of the trigonal system and T and T_h of the cubic system. The non-vanishing stress-optical coefficients were also worked out directly for all the 32 classes and the findings of the group theoretical method were confirmed. On the other hand, the same method, when applied to the elastic and optical coefficients and later to derive the number of independent constants needed to describe the piezo-electric and electro-optical Kerr effects, optical activity and pyro-electricity in crystals (Saksena, 1944; Suryanarayana, 1945, 1946) gave results which agreed with the known numbers for the respective phenomena.

The present experimental investigation relating to the photo-elastic behaviour of certain crystals, is undertaken to clear the existing discrepancy. The results obtained are in entire agreement with the findings of the group theoretical method.

2. Choice of the Material

As mentioned above, the T_h class of the cubic system is a case in which, while Pockels gave three constants in common with the other classes of this system, the theory developed by Bhagavantam requires four constants. Of the cubic crystals with which Pockels himself had worked, only two, namely potassium alum and ammonium alum, belong to the T_h class (Wyckoff, 1931). But Pockels had not determined the constants completely, on account of inhomogeneity of the material he worked with (*vide* Pockels, *Lehrbuch der Kristalloptik*, 1906, p. 480, foot-note 2). The original paper of Pockels (1892) dealing with the alums has not been available to the authors, and we are unable to find out if he has himself noticed any

discrepancies with the theory. Single crystals of potassium alum of optical quality could be grown to the necessary sizes and as the substance is quite stable under normal atmospheric conditions and in view of the fact that Pockels had worked with it, potassium alum is chosen for our investigations.

3. Theoretical Considerations

The non-vanishing stress-optical coefficients for T and T_h classes are given by the equations (1),

$$\begin{aligned} B_{11}-B &= -(q_{11}P_{xx}+q_{12}P_{yy}+q_{13}P_{zz}); \quad B_{23}=-q_{44}P_{yz}; \\ B_{22}-B &= -(q_{13}P_{xx}+q_{11}P_{yy}+q_{12}P_{zz}); \quad B_{31}=-q_{44}P_{zx}; \\ B_{33}-B &= -(q_{12}P_{xx}+q_{13}P_{yy}+q_{11}P_{zz}); \quad B_{12}=-q_{44}P_{xy}; \end{aligned} \tag{1}$$

consisting of four independent constants, while according to Pockels $q_{12}=q_{13}$ leaving only three constants. Here, $B=\frac{1}{n^2}$, $B_{11}=\frac{1}{n_{11}^2}$, etc., where n is the refractive index of the undeformed cubic crystal, n_{11} etc., are the components describing the Fresnel ellipsoid in the deformed condition, $P_{xx},\ldots P_{xy}$ are the components of stress tensor and q_{11}, q_{12}, q_{13} and q_{44} are the stress-optical coefficients, all referred to the crystallographic axial system.

One direct and striking result of the non-equivalence of q_{12} and q_{13} is that the crystal becomes biaxial by a simple compression along a cube axis, say Z-axis, instead of becoming uniaxial as in the case of the classes T_d, O and O_h, where $q_{12}=q_{13}$. This point could be settled by a direct observation of the double refractions, or more precisely, the path differences per unit pressure and unit length of the light beam in the crystal, between two beams, one vibrating along and the other perpendicular to, the direction of the pressure for light propagated along the other two cube axes, say X and Y, *i.e.*, when the observations are made along these axes. These two path differences should be different if the crystal has four independent constants. Again, for the same direction of pressure, the path differences should be identical when observations are made parallel to [110] and [$\bar{1}$10] directions.

The expressions for the path differences for the various cases are given in Table I. The derivations follow well-known principles, employed earlier by Pockels.

If $q_{12}=q_{13}$, expressions in column 4 become identical with those given in column 5. An examination of the table shows that two rectangular parallelopipeds with their lengths parallel to a cube axis, say [001], and the other two edges parallel (1) to the cube axes [100] and [010], and (2) to the [110] and [$\bar{1}$10] directions, will provide evidence in favour of the one or the other scheme with internal checks also. There is no difference between

TABLE I

No.	Direction of pressure	Direction of observation	Expression for path-difference for T and T_h classes	Expression according to Pockels' scheme
1	[001]	[100]	$\frac{2}{n^3}(q_{11}-q_{12})$	$\frac{2}{n^3}(q_{11}-q_{12})$
2	[001]	[010]	$\frac{2}{n^3}(q_{11}-q_{13})$	,,
3	[001]	[110]	$\frac{1}{n^3}(2q_{11}-q_{12}-q_{13})$	,,
4	[001]	[$\bar{1}$10]	,,	,,
5	[111]	[$\bar{2}$11]	$\frac{2}{n^3}q_{44}$	$\frac{2}{n^3}q_{44}$
6	[111]	[01$\bar{1}$]	,,	,,

the two schemes in case pressure is along the cube diagonal, *i.e.*, [111] direction.

4. EXPERIMENTAL ARRANGEMENTS

All the prisms needed were cut and polished from crystals grown in this laboratory by slow evaporation over a period of three months, of aqueous solutions of B. D. H. Analar potassium alum. Half a dozen crops were raised and the material was chosen from the best crop. Only the most perfect single crystals without flaws were selected, regard being shown for flawlessness and not so much for large size. Almost all the specimens chosen had very well-developed cube and dodecahedral faces in addition to the usual octahedral faces. All the prisms of lengths from 8 to 12 mm. and lateral dimensions 3 to 4 mm., have at least one of their ends terminated on a natural face. The four longer faces are ground parallel to natural edges along the required directions. The orientations are accurate to within 1°. None of the prisms show any double refraction under crossed Nicols in an unstrained state.

Light from a sodium vapour lamp is condensed by a lens on the slit of a collimator. The emergent parallel beam of light passes through a Nicol mounted on a circular scale with vernier, the vibration direction of the Nicol being maintained at $+45°$ or $-45°$ to the vertical. The beam then passes through the crystal prism into a Babinet compensator, the principal axes of which are vertical and horizontal. The light after passing through the compensator is observed through an eye-piece containing a Nicol crossed with the polarizer and the usual Babinet fringes are obtained. When the crystal prism is compressed, the fringes shift one way or the other and the magnitude of the shift is a measure of the path difference produced

between the horizontally and vertically vibrating beams of light passing through the compressed crystal.

Compression is produced by a lever arrangement. Four fine v-grooves perpendicular to the length of the bar are marked on a cold steel bar $17'' \times \frac{1}{2}'' \times \frac{1}{2}''$, two on the upper and two on the lower side. In the upper groove A near one end sits a knife-edge fixed in a vice firmly clamped to a massive table, the groove B at the other end, distant 16″ from the first groove, being used for the knife-edge carrying weights. Two grooves on the lower side of the bar, at distances 2″ and 4″ from the groove A, to take the knife-edge on the crystal prism, give a mechanical advantage of about 8 and 4 as the case may be. The knife-edge which rests on the prism has a lead plate of 2 mm. thickness cemented to its base, of dimensions $1 \cdot 2 \times 1$ cm., to help distribute the load uniformly. The lower end of the prism rests on a horizontal solid metal support on which a small rubber washer 1 mm. thick is placed. The knife-edges are of spindle steel.

The knife-edge is placed symmetrically over the prism held vertical, with the required edge parallel to the light beam, on the metal support and the lever placed horizontally such that the two knife-edges are engaged in the grooves. A black paper slit stuck on to the metal support by soft wax just allows only the light coming through the prism.

With one of the prisms, measurements of the fringe shift for stresses about 0·25 kg./mm.^{2} and 0·5 kg./mm.^{2} are made and there was no appreciable departure from linearity. So, stresses upto about 0·5 kg./mm.^{2} only are used in all cases, except in the [111] direction. In this case, to obtain a displacement of the Babinet fringes which can be measured reasonably accurately, stresses upto 0·9 kg./mm.^{2} are employed. The displacement of the fringes is measured at the middle of the length of the prism, at three places along its breadth, namely near the left edge, the middle and the right edge. Before each set of observations, a preliminary measurement of the fringe displacement at the three positions is made and only when the distribution of the load is fairly uniform, the final measurements are made. In case the distribution is non-uniform, the position of the prism is adjusted until the distribution is fairly uniform. In each of the three positions, the polarizing Nicol and the analysing Nicol of the compensator, are turned through 90°, such that in the two positions, the incident light is polarized at $+45°$ and $-45°$ to the vertical. Thus in all, six measurements of the fringe displacement are made. For each of the six measurements, the initial position (without load) of the central Babinet fringe is taken twice before placing the load and twice after removing the load. The final position of

the Babinet fringe (on load) is obtained by four settings of the crosswire on the edge of the fringe. Thus each of the six measurements is the mean difference of four settings of the initial and final positions of the fringe. In the case of the [111] prism, each of the six measurements is the mean difference of six settings of the initial and final positions of the fringe. In none of the prisms was there any noticeable consistent residual double refraction after unloading (as deduced from the shift of the initial position).

The prism is then turned through 90° and the measurements are repeated similarly with identical load. Specimen observations for one of the prisms are given later in the paper.

To determine the absolute value of the stress-optical constants, a measure of the absolute change in the refractive index for vertically or horizontally polarized beam of light is needed. The method adopted by Pockels for other crystals was to measure the absolute path retardation by an interferometric method using two equal plane parallel prisms of the crystal in the two beams of the interferometer. When one of the prisms is compressed, the shifts in the fringes of the interferometer for light vibrating vertically and horizontally give a measure of the absolute changes in the refractive index for the two beams, when account is taken of the increase in the thickness of the prism by compression. In the absence of plane parallel prisms, the crystal itself can be used as an interferometer by forming localised interference fringes in the crystal itself, as has been done by Ramachandran (1947) recently in his determination of the photo-elastic constants of diamond.

The arrangement adopted is to work a pair of surfaces of the prism to get reasonably widely separated localised fringes, *i.e.*, curves of equal thickness, with reflected light. If light is reflected at the usual 45° angle at a glass plate, the observation of the shift of the fringes is not possible when the light is vibrating horizontally, because of the very low intensity. So, light is reflected at an angle of about 10° on to a pair of faces of the prism and the localised fringes formed by reflection of the beam at the two surfaces, are observed through a microscope. In obtaining the fringes, thicknesses of the crystal which give rise to destructive interference between the D_1 and D_2 lines are to be avoided. The microscope is focussed on a reference mark on the crystal itself and the movement of the fringes on loading is to be judged with reference to this mark. The shifting of the fringes is the combined result of the change in the thickness of the crystal and the change in the refractive index. Because of the low value of the elastic constants, a shift of one complete fringe could be produced in alum by

stresses of the order of 0·3 kg./mm.^{2} The procedure adopted is to note the load for a shift of a complete fringe for light beams polarized vertically and horizontally. The sign of the shift, namely, whether the order of interference is decreasing or increasing at the point under observation, settles the sign of the stress-optical constants unambiguously.

In order to provide checks as well as to study any possible effect of the ratio of the length to the lateral dimensions, on the observed stress-optical coefficients, two prisms of different dimensions are taken for each orientation for pressures in the [001] direction.

A description of the five prisms employed in the investigation is given in Table II.

TABLE II

Description of the prisms employed

No. of prism	Length, l		Breadth, b		Thickness, d	
	cm.	$\parallel^l$ to	cm.	$\parallel^l$ to	cm.	$\parallel^l$ to
I ..	1·17	[111]	0·408	$[\bar{2}11]$	0·360	$[01\bar{1}]$
II ..	0·78	[001]	0·293	[100]	0·294	[010]
III ..	0·86	[001]	0·409	[100]	0·407	[010]
IV ..	1·26	[001]	0·412	[110]	0·348	$[\bar{1}10]$
V ..	0·78	[001]	0·403	[110]	0·291	$[\bar{1}10]$

5. RESULTS

(*a*) *Determination of* $(q_{11}-q_{12})$, $(q_{11}-q_{13})$ *and* q_{44}.

Complete observations with the Babinet compensator for Prism II are given as an example in Table III. The results on all five prisms are given in detail in Table IV.

In prism III, observations along [100] and [010] with a load of 1 kg. were made first and then the observations with 2 kg. It may be noted that the shifts for 2 kg. are very slightly less than twice the shifts for 1 kg., suggesting a small residual double refraction. The difference however, is of the same order as the experimental errors themselves, so that we can assume that upto stresses of the order of 0·5 kg./mm.^{2} the condition of linearity is satisfied.

The fringe width of the Babinet compensator is 144·6 divisions, which corresponds to a path retardation of one wavelength of sodium light. The

TABLE III

TABLE III

Observations on Prism II

Load = 1 kg. ; mechanical advantage = 3·973

The readings are head scale divisions of the Babinet compensator. 50 head scale divisions equal 1 main scale division

Observation along [010], 0·294 cm.

	Middle				Left				Right				
	+ 45°		− 45°		− 45°		+ 45°		+ 45°		− 45°		
	Initial	Final	I	F	I	F	I	F	I	F	I	F	
1	15 27	15 01·5	15 30	15 07	15 29·5	15 04	15 30	15 05·5	15 32	15 08	15 32	15 07	
2	28·5	03	30	07	28	03·5	30·5	05	30	11	32·5	09·5	
3	29	01·5	28	07	30·5	03	28	05·5	31	10	31·5	09	
4	26	02	30·5	07	30	03·5	23·5	05	31	10	30	10	
Mean	27·62	02	29·62	07	29·5	03·5	29·25	05·25	31	09·75	31·5	08·88	
Diff.	25·62		22·62		26·0		24·0		21·25		22·62		
Mean	24·12				25·0				21·94				Mean = 23·69

Observation along [100], 0·293 cm.

	Middle				Left				Right				
	− 45°		+ 45°		+ 45°		− 45°		− 45°		+ 45°		
	I	F	I	F	I	F	I	F	I	F	I	F	
1	15 25·5	14 46	15 25·5	14 48	15 23·5	14 48	15 25·5	14 48	15 26·5	15 02	15 30	14 47·5	
2	24·5	15 00	25·5	46	25·5	15 00	25·5	15 01	26·5	03	28	15 02	
3	25·5	14 48	26·5	15 00	24·0	00	23	14 47	25·5	02	29·5	00·5	
4	25·5	48	25·5	14 46	25·5	14 47	26	49	24	02	27·5	02·5	
Mean	15 25·25	14 48	15 25·75	14 47·5	15 24·62	14 48·75	15·25	14 48·75	15 25·62	15 02·25	15 28·75	15 00·62	
Diff.	27·25		28·25		25·87		26·25		23·37		28·13		
Mean	27·75				26·06				25·75				Mean = 26·52

TABLE IV

Photo-elastic constants of potassium alum: observations with compensator

Prism No.	Observation: Parallel to	Observation: cm.	Load in kg.	Mechanical advantage of lever	Shift of the Babinet fringe in divisions of head scale: Left + 45°	Left − 45°	Middle + 45°	Middle − 45°	Right + 45°	Right − 45°	Mean	Stress-optical constants in units of 10^{-5}	Expression for the *constent $\times \frac{\pi^2}{2}$
I	[211]	0·408	1·6	7·90	7·9	8·3	7·9	8·0	6·6	10	8·12	0·63	(q_{44})
	[011]	0·360			4·9	6·2	8·5	9·0	8·2	7·9	7·45	0·65	,,
II	[010]	0·294	1·0	3·973	24·0	26·0	25·62	22·62	21·25	22·62	23·69	4·79	$(q_{11}-q_{13})$
	[100]	0·293			25·87	26·25	28·25	27·25	28·13	23·37	26·52	5·38	$(q_{11}-q_{12})$
III	[010]	0·407	1·0	,,	14·75	15·45	18·35	16·2	17·4	15·9	16·34	4·58	$(q_{11}-q_{13})$
	[010]		2·0	,,	33·00	33·75	31·63	34·12	30·13	30·88	32·26		
	[100]	0·409	1·0	,,	18·25	17·88	17·50	19·00	19·22	19·25	18·52	5·17	$(q_{11}-q_{12})$
	[100]		2·0		37·4	35·1	35·25	37·65	36·37	37·15	36·49		
IV	[110]	0·412	1·6	,,	33·75	35·12	36·0	33·87	29·5	28·63	32·81	4·93	
	[110]				30·38	34·25	35·13	35·00	31·63	31·62	33·01	4·96	$(2q_{11}-q_{12}-q_{13})/2$
	[110]	0·348			29·88	30·87	28·37	28·63	26·13	26·75	28·44	5·06	
V	[110]	0·403	1·4	,,	31·0	31·37	37·25	32·88	34·13	36·75	33·90	4·86	,,
	[110]	0·291			24·37	22·87	21·87	23·76	24·75	25·88	23·92	4·75	

stress-optical constants are calculated as follows. From the mean shift of the Babinet fringe, the path difference δ corresponding to unit stress (1 kg./mm.^{2}) and unit length (1 cm.) of light beam in the stressed crystal is calculated, noting that the path difference is $5{\cdot}893 \times 10^{-5}$ cm. for a shift of 144·6 divisions. The stress-optical constant in the corresponding direction of observation is $= \frac{2}{n^3}\delta$, where δ is the path difference $(n_x - n_z)$ between the horizontally and vertically vibrating light beams. In the above experiments, the shift was always in the same direction as for common glass, *i.e.*, the crystal becomes negative uniaxial when compressed along the trigonal axis. Hence, the sign of the constants q_{44}, $(q_{11} - q_{12})$ and $(q_{11} - q_{13})$ is negative.

An examination of Table IV reveals the following facts:

(1) In prism II, stress-optical constants in the X and Y directions differ from each other by 12% which is much more than any possible experimental error.

(2) The two values bracketed together in prism IV, are the values of one and the same constant when observed along two directions and differ by 2% which is the order of the experimental error. The mean of these values, namely, 5·01 differs by 1·5% from the mean (5·085) of the two constants from prism II, which difference is again of the order of the experimental error.

(3) In prism III, while the two constants differ from each other again by about 12%, the absolute values of the constants for this prism are smaller by 4% than the corresponding values for prism II.

(4) In prism V, the two values differ by about 2%, which is, as mentioned above, within the experimental error and the mean of these values, namely, 4·805 differs by 1·5% from the mean (4·875) of the constants for prism III. Again, the absolute value of the mean value for $(2q_{11} - q_{12} - q_{13})$ from this prism is smaller by 4% than the corresponding value from prism IV.

(5) The first two rows under prism IV, show the consistency with which the constants are obtained for two independent observations, the first row being obtained when the distribution of stress is more non-uniform than in the case of the second row.

In view of the above, it can be stated with confidence, that the difference between the constants $(q_{11} - q_{12})$ and $(q_{11} - q_{13})$ in this case is about 12% and quite real. Hence the description of the photo-elastic behaviour

of potassium alum needs four independent constants and not three because $q_{12} \neq q_{13}$.

The consistent differences between the values for prisms II and III and the corresponding values for prisms IV and V, have to be attributed to the effect of the relative dimensions of the prisms. We can see that the conditions for de Saint-Venant's principle to apply are better satisfied in the case of prisms II and IV than in prisms III and V. Hence, the values from prisms II and IV are adopted as the better approximations to the actual values. (This principle of de Saint-Venant states that, at a sufficient distance from the point of application of a load, the stress system depends only upon the statical resultant of this load and not upon its particular mode of application.)

Giving a weightage of 2 to the mean value of $(2q_{11} - q_{12} - q_{13})$ from prism IV and unit weight to the values of $(q_{11} - q_{12})$ and $(q_{11} - q_{13})$ from prism II, the most probable values of $(q_{11} - q_{12})$ and $(q_{11} - q_{13})$ are deduced by forming normal equations from the above observational equations. They are $(q_{11} - q_{12}) = -5{\cdot}32 \times 10^{-5}$ and $(q_{11} - q_{13}) = -4{\cdot}73 \times 10^{-5}$. It is from these values, that $(p_{11} - p_{12})$ and $(p_{11} - p_{13})$ are calculated in a later para. The values from prisms III and V will be 4% smaller but they also point out, as mentioned above, that the stress-optical constants are four and not three. The mean of q_{44} is $-0{\cdot}64 \times 10^{-5}$.

(*b*) *Determination of the absolute stress-optical coefficients* q_{11}, q_{12} *and* q_{13}.

For this purpose, prism II is used. The side which was 0.294 cm. long was reduced to 0·277 cm. and a set of distorted elliptical fringes were obtained in that direction. The other dimension 0·293 was reduced to 0·289. The crystal was acting like a double convex lens of a very large focal length in the direction of observation. Two suitable marks near the middle of the vertical height were chosen and the loads for a shift of a complete fringe at each of those marks, for light vibrating vertically and horizontally are noted. The spacing of the fringes is actually about 1/5 mm. and the dark bands themselves were, for well-known reasons, not very sharp. On this account, a change of about 50 gm. in a load of 800 gms. will just escape notice. With these limitations, at both the points, the loads for a shift of one complete fringe for vertically and horizontally vibrating beams of light, are 800 gm. and 600 gm. respectively, when the mechanical advantage of loading is 3·793. Any slight non-uniformity of stress existing escapes notice. The shift was away from the centre of the fringe system and hence, at the point of observation, the order of interference was increasing.

The absolute values of the constants are calculated from the equations

$$n - n_z = \frac{\lambda}{2t_2}\left[\frac{2n}{\lambda}(t_2 - t_1) - \delta n\right] \text{ and}$$

$$q_{11} = (n - n_z)\frac{2}{n^3 P_{zz}}.$$

Here, n is the refractive index of the undeformed crystal, n_z the refractive index in the stressed crystal for light with vibration direction vertical, $(t_2 - t_1)$ the increase in thickness of the crystal along the direction of observation for the corresponding load, λ is the wavelength of the light, δn is the increase in the order of interference at the point of observation and P_{zz} is the stress producing the shift. Here, δn is $+1$ and n, the refractive index is taken as 1·456 (Landolt Bornstein Tables, Zweiter Erganzungsband, Zweiter Teil, p. 917) for sodium light. Similar equations which hold for light vibrating horizontally are

$$n - n_x = \frac{\lambda}{2t_3}\left[\frac{2n}{\lambda}(t_3 - t_1) - \delta n\right] \text{ and}$$

$$q_{13} = (n - n_x)\frac{2}{n^3 P_{zz}}.$$

The value of P_{zz} here is different from the P_{zz} given earlier.

The elastic constants of potassium alum have been determined by Voigt (1919) and recently in this laboratory by Sundara Rao (1947). The necessary constants are given in Table V.

TABLE V

Unit	10^{11} dynes/cm.^{2}			10^{-12} cm.^{2}/dyne	–
Constant	C_{11}	C_{12}	C_{44}	S_{11}	σ
Voigt ..	2·43	1·009	0·843	5·441	0·2933
Sundara Rao ..	2·56	1·07	0·86	5·182	0·2947

The mean of these two sets has been adopted in this paper, after converting them into units of kg./mm.^{2}, for determining the change in thickness of the prism, as well as for evaluating the strain-optical coefficients.

Employing the data given above, we get

$$q_{11} = +3{\cdot}0 \times 10^{-5} \text{ and } q_{13} = +8{\cdot}9 \times 10^{-5},$$

giving a difference $(q_{11} - q_{13})$ of $-5{\cdot}9 \times 10^{-5}$ against the most probable value of $-4{\cdot}73 \times 10^{-5}$ given earlier. It must be pointed out that a value

of 750 gm., for example, instead of the 800 gm. for the load used, brings q_{11} to $+4{\cdot}1\times 10^{-5}$ from $3{\cdot}0\times 10^{-5}$. Hence, in view of the facts stated earlier about the fringe displacements, the values of q_{11} and q_{13} can be regarded as giving the order of magnitude only. Provisionally the values may be taken as

$$q_{11}= 3{\cdot}6\times 10^{-5},\ q_{13}= 8{\cdot}3\times 10^{-5} \text{ and } q_{12}= 8{\cdot}9\times 10^{-5}$$

as obtained by forming normal equations after giving any large weight for the Babinet observations compared to the observations on absolute values.

(*c*) *Evaluation of the strain-optical coefficients.*

The four strain-optical coefficients are calculated from the equations

$$p_{11}= q_{11}c_{11}+(q_{12}+q_{13})\,c_{12}; \qquad p_{44}= q_{44}c_{44};$$
$$p_{12}= q_{12}c_{11}+(q_{11}+q_{13})\,c_{12}; \qquad (p_{11}-p_{12})=(q_{11}-q_{12})\,(c_{11}-c_{12});$$
$$p_{13}= q_{13}c_{11}+(q_{11}+q_{12})\,c_{12}; \qquad (p_{11}-p_{13})=(q_{11}-q_{13})\,(c_{11}-c_{12});$$

adopting the mean values

$$c_{11}= 2{\cdot}55\times 10^{3}\ \text{kg./mm.}^2,\ c_{12}= 1{\cdot}06\times 10^{3}\ \text{kg./mm.}^2$$

and $c_{44}= 0{\cdot}866\times 10^{3}$ kg./mm.^{2}.

The values are

$(p_{11}-p_{12})=$	$-0{\cdot}0792$	$p_{11}=$	$+0{\cdot}27$
$(p_{11}-p_{13})=$	$-0{\cdot}0704$	$p_{12}=$	$+0{\cdot}35$
$p_{44}=$	$-0{\cdot}0056$	$p_{13}=$	$+0{\cdot}34$

6. Discussion of the Results

The values of Pockels may be compared with the above values. His q_1 which is $(q_{11}-q_{12})$ in our notation, is given as $-4{\cdot}30$ (Pockels, 1906; Szivessy, 1929). As mentioned above, the original paper of Pockels was not available to the authors, but from his other papers on rocksalt and fluorite, we infer that it may be the mean of the two constants $(q_{11}-q_{12})$ and $(q_{11}-q_{13})$ in our notation. The value is considerably smaller in magnitude than our value $-5{\cdot}02$. His value of q_{44} is $-0{\cdot}455$ to be compared with our $-0{\cdot}64$ which is also higher. The amount of double refraction produced when the crystal is compressed along a cube axis is about 8 times as large as that produced when it is compressed along the cube diagonal. Wertheim also has measured the double refraction in alum (Coker and Filon, 1931) earlier than Pockels but neither the direction of pressure nor that of observation with reference to the crystallographic axes was given.

It may also be noted that the absolute stress-optical constants q_{11}, q_{12} and q_{13} for alum are the largest known of all cubic crystals so far studied.

In conclusion, it may be pointed out that four independent constants are required for describing the photo-elastic behaviour of potassium alum which belongs to the class T_h, on account of the fact that in this class the cube axes are only digonal and not tetragonal. Apparently, it is this point that Pockels missed. Now, it can be stated as a general rule applicable to cubic crystals of all the 5 classes, that a pressure along any axis of trigonal or tetragonal symmetry makes the crystal optically uniaxial and a pressure along any diagonal axis, or a general direction, makes the crystal biaxial. This can easily be understood if it is remembered that the symmetry properties of the optical ellipsoid follow the symmetry of all the other physical properties, according to Neumann's principle.

7. Summary

To test an earlier prediction by Bhagavantam based on a group theoretical method, that the T and T_h classes of the cubic system need four independent constants instead of three, for describing their photo-elastic properties, crystals of potassium alum belonging to the T_h class are studied completely. It has been found that the crystal needs four independent constants and all the four stress-optical constants of alum are determined for the first time. For sodium D lines, they are $(q_{11}-q_{12})=-5.32$, $(q_{11}-q_{13})=-4{\cdot}73$, $q_{44}=-0{\cdot}64$, $q_{11}=+3{\cdot}6$, $q_{12}=+8{\cdot}9$, $q_{13}=+8{\cdot}3$, all in units of 10^{-5} when stress is expressed as kg./mm.^{2} and the path difference in cm. The values of the strain-optical coefficients are $(p_{11}-p_{12})=-0{\cdot}0792$, $(p_{11}-p_{13})=-0{\cdot}0704$, $p_{44}=-0{\cdot}0056$, $p_{11}=+0{\cdot}27$, $p_{12}=+0{\cdot}35$, $p_{13}=+0{\cdot}34$.

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THE SCATTERING OF POLARISED LIGHT BEAMS IN BIREFRINGENT SOLIDS

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1. Introduction

The present Lord Rayleigh (1919) observed that when a beam of plane polarised white light is sent along the optic axis of a crystal of smoky quartz, its track, when viewed in a direction transverse to the beam, exhibits coloured bands. The phenomenon is obviously connected with the rotatory power of quartz which varies with the wavelength and has its origin in the polarisation of the Tyndall scattering by the inclusions present in the crystal. The phenomenon has also been photographed in perfectly clear quartz by the author (1947) using monochromatic ultra-violet λ 2537 radiation of the mercury arc, the diffusion of light in this case having its origin in the atomic vibrations in the crystal. The effect is then much more striking owing to the high rotatory power of quartz in the ultraviolet. This investigation suggested the study of the scattering of plane-polarised light beams in birefringent solids which are not optically active.

A beam of plane-polarised light traversing a birefringent crystal divides into two beams polarised in perpendicular planes. These travel with different velocities but being everywhere coherent, they would combine and give a single elliptically polarised light beam, in which, however, the constants of ellipticity change periodically along the path. Hence, the track of the beam made visible by the scattered light should, in general, exhibit bands of fluctuating intensity. However, the case differs from that of optically active solids in several respects. *Firstly*, along the directions of single wave velocity, the light travels without undergoing any change in the state of its polarisation. There would then be no fluctuations in the intensity of the scattered light along the track. *Secondly*, the band width would vary with the direction of propagation. *Thirdly*, the azimuth of the electric vector in the incident light beam as well as the azimuth of observation are both important. When the incident light vector coincides with one of the principal planes of the crystal, the beam travels without any alteration in its state of polarisation and hence no fluctuations in its intensity would be observed

in light scattering. On the other hand, the maximum changes in its state of polarisation would occur when the electric vector is inclined at 45° to the principal planes. In this case, the beam would be plane-polarised, alternately in and at right angles to the original azimuth. Viewed in either of these planes, the track would show the maximum fluctuations in intensity, while intermediately the track would appear of uniform brightness.

Now the distance traversed inside the crystal for a complete cycle to occur depends on the birefringence, and unless the length of the periodic cycle of changes is at least a millimetre or two, it would be difficult to observe the fluctuations of intensity along the track. Hence, crystals with small birefringence would be most suited for the experiment. However, even with crystals which are strongly birefringent, this difficulty could be overcome by sending the light beam very near to the optic axis. For example, with calcite which has a very large birefringence, a beam making an angle of 2° to the optic axis should give a band width of the order of a millimetre. Specimens to be suitable for exhibiting these phenomena should be large and perfectly clear single crystals preferably transparent to the ultraviolet λ 2537 radiation of the mercury arc, as that could then be employed to record the effects photographically. As the birefringence of crystals, in general, varies but little with wavelength, the band width would be proportional to the wavelength. If the single crystals are shaped into spheres and polished, both the direction of propagation and the azimuth of observation could be varied at ease for the convenient study of the phenomenon.

Pending the preparation of such crystal spheres suitable for the work, the phenomenon has been observed and studied by the author in plates of synthetic organic glasses. These often exhibit permanent strains and hence behave like uniaxial or biaxial crystals with very small birefringence. They also scatter light strongly, such scattering being well polarised. Employing sunlight filtered through a violet glass or monochromatic sodium yellow light λ 5893, all the points stated above have been successfully illustrated in the observations using them. Photographs, showing the effects, are reproduced on the Plates.

2. Description of the Phenomena

A narrow beam of plane polarised sunlight, filtered through a violet glass, was sent perpendicular to the optic axis of a rectangular plate of colourless and transparent plexiglas. The plate is a uniaxial solid with very small birefringence and its optic axis is parallel to its thickness. Three photographs of the track, taken in an azimuth inclined to the optic axis, are reproduced in Figs. 1 (*a*), 1 (*b*) and 1 (*c*), Plate III, the exposure in each

case being one minute. In the case of Figs. 1 (*a*) and 1 (*b*), the incident light vector was inclined at about − 40° and + 40° to the optic axis respectively. These figures show fluctuations in intensity along the track and there is just about one band and a half for 9 centimetres. The maxima of intensity of Fig. 1 (*a*) coincide with the minima of Fig. 1 (*b*) and *vice versa*. Owing to the refraction of light taking place when the diffused light emerges obliquely to the face normal to the optic axis, the incident light beam was only polarised with the electric vector at an angle of 40° to the optic axis and not at the optimum angle of 45° to the axis. The azimuth of observation in each case was about 75° to the axis. In the case of Fig. 1 (*c*), the incident light vector was parallel to the optic axis, and hence the track is of uniform brightness.

Now, instead of varying the azimuth of the incident light vector, if that of observation is varied the same sequence of phenomena is obtained, provided that the incident light vector is at 45° to the optic axis. When white light is used, coloured bands are seen in the proper azimuths since the bandwidth varies with the wave-lengths.

In the case of two yellow plates of transparent bakelite, the effect has been photographed and is reproduced in Figs. 2 (*a*), 2 (*b*) and 2 (*c*) in the case of one and in Figs. 3 (*a*), 3 (*b*) and 3 (*c*) in the other case. As these plates have a larger birefringence, they exhibit a number of bands instead of just one and a half as in the case of plexiglas. To prevent overlapping of higher orders of the bands, the monochromatic yellow light of the sodium lamp was used in these two cases, and the tracks were photographed in about 2 to 4 hours using HP3 plates. Even in monochromatic light, the higher orders of the bands lose gradually their clarity. They are also curved and their curvature varies with their position. All this is due to the irregular birefringence of the bakelite. In spite of the yellow light employed, the intensity along the tracks gradually falls off with the advance of the beam, due to the absorption of light by the bakelite.

In conclusion, the author wishes to thank Sir C. V. Raman for his constant encouragement and guidance throughout the course of the investigation.

3. Summary

As a plane-polarised light beam advances inside a birefringent solid, its state of polarisation, in general, undergoes a periodic cycle of changes. In light-scattering transverse to the beam, these changes manifest themselves as fluctuations in intensity along the track; there would be one band for one complete cycle. The bands would be most marked when *both* the azimuth

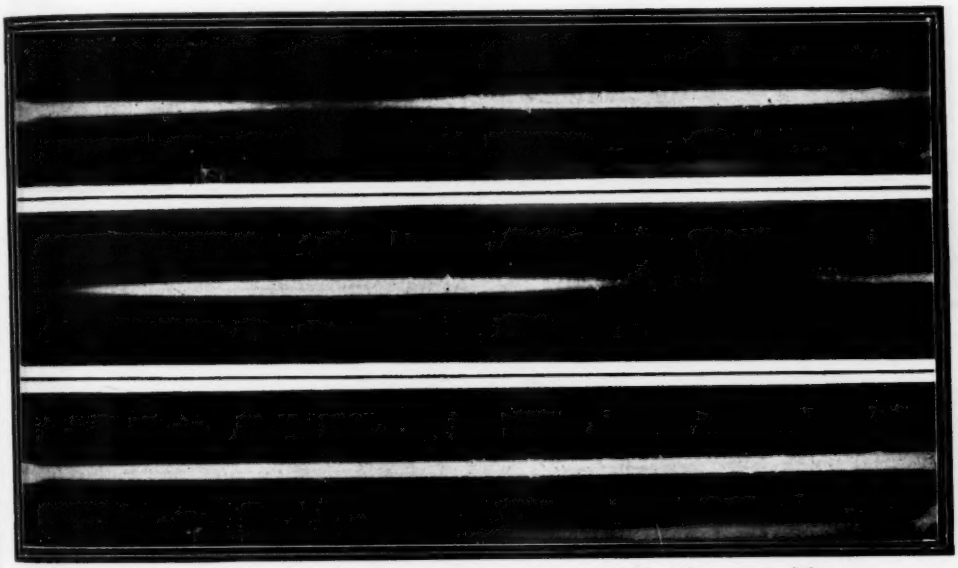

FIG. 1. Tracks of polarised violet beam traversing birefringent plexiglas

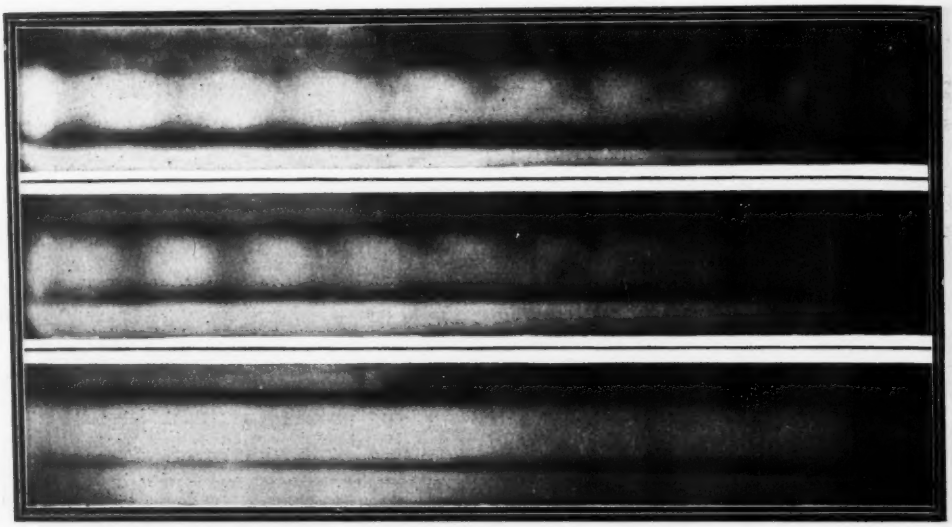

FIG. 2. Tracks of polarised λ 5893 beam traversing birefringent bakelite I

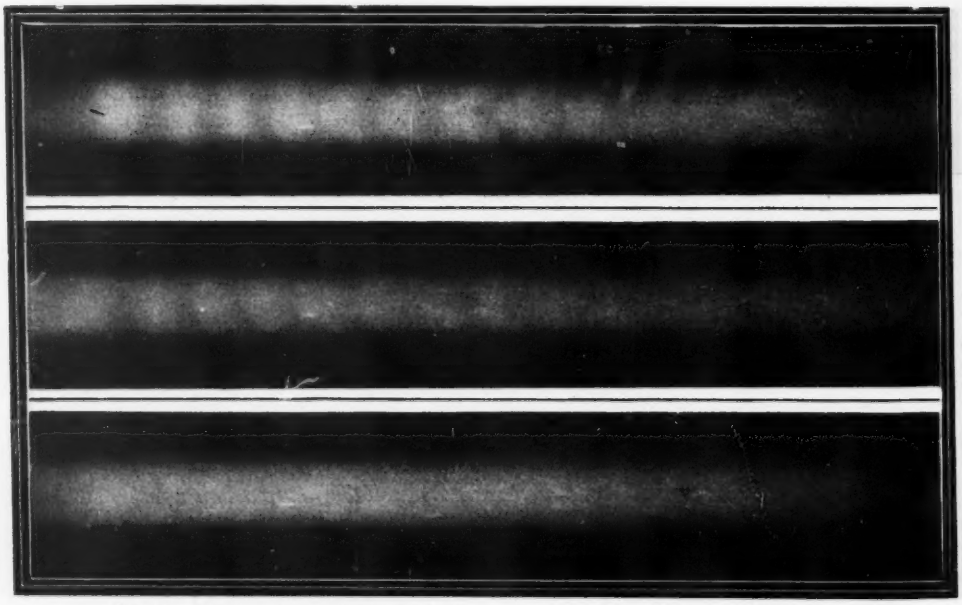

FIG. 3. Tracks of polarised λ 5893 beam traversing birefringent bakelite II

of the incident light vector as well as that of observation are inclined at 45° to the principal planes of the solid. On the other hand, the fluctuations in intensity would disappear when *either* of the azimuths coincide with one of the principal planes. Using three synthetic organic glasses with permanent strains and hence behaving like uniaxial or biaxial crystals with very small birefringence, these effects have been studied and photographs, showing these, are reproduced in the paper.

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BIREFRINGENCE OF CRYSTALS AND ITS TEMPERATURE-VARIATION

II. Sodium and Potassium Nitrates

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1. Introduction

In Part I of this series (Ramachandran, 1947 *g*, which will be referred to hereafter as B1), an attempt has been made to apply dispersion theory to the explanation of birefringence of crystals. It is suggested that birefringence arises from the existence of polarised electronic transitions, so that the probability of transition is different for different directions of the incident electric vector. Thus, the dispersion formulæ for the three principal indices of a biaxial crystal would contain the same dispersion frequencies; but the oscillator-strengths would be different. The idea was applied to the cases of calcite and aragonite in B1 and shown to fit the experimental data. The interesting fact emerged that the strong birefringence in both the crystals was due to the high polarisation of the nearest ultra-violet dispersion frequency at 1535 A.U., whose activity was almost completely confined to the plane of the CO_3 ions. The same ideas have been here applied to sodium and potassium nitrates, with exactly similar results. A major part of the birefringence of the nitrates is to be attributed to a highly polarised electronic transition at about 2000 A.U. which is practically inactive in a direction at right angles to the plane of the NO_3 ion.

In the case of the carbonates we have no direct verification of the differential activity of the dispersion frequency at 1535 A.U. in directions parallel and at right angles to the plane of the CO_3 ion. However, the work of K. S. Krishnan and his collaborators has revealed some evidence to show that such a phenomenon actually occurs in the nitrates and also in aromatic organic compounds such as chrysene, naphthacene, etc. The nitrate ion has a feeble absorption centred about 3000 A.U. This is however practically ineffective in dispersion as found by Krishnan and Das Gupta (1933) in crystalline potassium nitrate. They also found that the coefficient of absorption over this band in this salt is much larger when the electric vector

lies in the plane of the NO_3 ion than at right angles to it. A similar result was also found at the beginning of the strong continuous absorption beyond 2500 A.U. Highly polarised fluorescence and absorption have been observed by Krishnan and Seshan (1934, 1939) in chrysene, naphthacene and fluorene in which the electronic transition is completely confined to the plane of the carbon rings.

In B1, the author's theory of thermo-optic behaviour for isotropic solids (*cf.* Ramachandran, 1947 *a–f*, referred to below as A1–A6) was extended for birefringent crystals, and applied with success to explain the dn/dt data for calcite and aragonite. The theory was particularly successful in explaining the interesting difference in thermo-optic behaviour between the two crystals, which are so allied in structure as well in optical properties, *viz.*, that while dn/dt is positive for both the indices of calcite, it is negative for all the indices of aragonite. The difference arises from the much larger thermal expansion of the latter, which gives rise to a large negative contribution to dn/dt. Unfortunately, no measurements are available of the temperature-variation of the refractive indices of nitrates so that a further confirmation of the theory is not possible. However, dn/dt has been calculated for $NaNO_3$ following the analogy of calcite in Section 3.

2. Development of the Dispersion Formulæ

The dispersion data available for the two crystals under study are neither as accurate nor as plentiful as those for calcite and aragonite. The two refractive indices of $NaNO_3$ have been measured for the E, D and B Fraunhofer lines by Schrauf (1860) and for a number of wavelengths between $0{\cdot}668$ and $0{\cdot}434\,\mu$ by Merwin (1930). The agreement between the two for the D line is good enough for the extraordinary ray, but is rather bad for the ordinary ray. However, Merwin's data are nearer to the measurements of Cornu (1867) and Kohlrausch (1878). The dispersion formulæ for $NaNO_3$ have been developed here on the basis of Merwin's measurements.

For potassium nitrate also, Schrauf (*loc. cit.*) has measured all the three indices for the E, D and B lines and Merwin (1930) for wavelengths from $0{\cdot}768$ to $0{\cdot}405\,\mu$. In addition, K. S. Krishnan and A. C. Das Gupta (1933) have measured n_1 and n_2 by interferometric methods from $0{\cdot}687\,\mu$ down to $0{\cdot}253\,\mu$. Although these measurements are based on Schrauf's values of the indices for the B and D lines and the indices have been measured only to 3 places of decimals below $0{\cdot}3\,\mu$, yet they are more useful than Merwin's for the present purpose, since they cover a wide range of wavelengths, almost up to the limit of transmission in the ultra-violet. We have only made use of these in deriving the dispersion formulæ for KNO_3.

As already mentioned, the nitrate ion in solution exhibits a feeble absorption centred about $0{\cdot}30\,\mu$ (which is almost inactive in dispersion in KNO_3) and then a continuous absorption with increasing strength towards shorter wavelengths beyond $0{\cdot}25\,\mu$. The first dispersion frequency of the two crystals was taken to be at 2000 A.U., inside this strong absorption. The second frequency in the dispersion formula was taken at 1100 A.U. The term due to a remote ultra-violet frequency was put equal to a constant term. The dispersion formula thus takes the form:

$$n^2 - 1 = a_0 + \frac{a_1 \lambda^2}{\lambda^2 - (0{\cdot}110)^2} + \frac{a_2 \lambda^2}{\lambda^2 - (0{\cdot}200)^2} - k\lambda^2, \qquad (1)$$

$k\lambda^2$ standing for an infra-red term. The accuracy of the data did not justify the explicit use of a dispersion frequency in the infra-red. The same ultra-violet frequencies were used for both KNO_3 and $NaNO_3$. They were in fact deduced from the data for KNO_3 and then adopted for $NaNO_3$. The data for the latter, being restricted to a small range of wavelengths could not have been used for obtaining the dispersion frequencies with any degree of accuracy. The values of a_0, a_1, a_2, k for the two crystals are given in Table I. In Table II, the refractive indices calculated from the formulæ are compared with the actual measurements.

TABLE I

	$NaNO_3$		KNO_3	
	ω	ε	1	2
a_0 ..	0·5320	0·4717	0·3710	0·4570
a_1 ..	0·4898	0·3057	0·4007	0·4324
a_2 ..	0·4362	0·0011	0·0007	0·3326
k ..	0·0560	0·0151	0·0155	0·0400

TABLE II. $NaNO_3$

Wavelength	ω		ε	
	Exp.	Cal.	Exp.	Cal.
H 434 ..	1·6126	1·6121	1·3404	1·3404
Hg 436 ..	1·6121	1·6115	1·3403	1·3403
H 486 ..	1·5998	1·6000	1·3384	1·3385
He 501 ..	1·5968	1·5972	1·3379	1·3379
Hg 546 ..	1·5899	1·5904	1·3365	1·3368
Hg 579 ..	1·5860	1·5865	1·3363	1·3359
Na 589 ..	1·5848	1·5853	1·3360	1·3358
H 656 ..	1·5791	1·5788	1·3347	1·3345
He 668 ..	1·5783	1·5778	1·3345	1·3342

KNO_3

Wavelengths in microns	n_1		n_2	
	Exp.	Cal.	Exp.	Cal.
0·2530	1·698	1·700	1·367	1·366
0·2600	1·671	1·673	1·364	1·364
0·2700	1·644	1·646	1·361	1·361
0·2800	1·624	1·626	1·358	1·359
0·2900	1·608	1·610	1·356	1·356
0·3000	1·5950	1·5965	1·3543	1·3544
0·3100	1·5861	1·5871	1·3526	1·3527
0·3200	1·5782	1·5785	1·3514	1·3513
0·3300	1·5703	1·5705	1·3499	1·3498
0·3500	1·5582	1·5581	1·3479	1·3473
0·3663	1·5502	1·5500	1·3460	1·3457
0·3969	1·5384	1·5382	1·3435	1·3432
0·4358	1·5279	1·5276	1·3410	1·3407
0·5270	1·5125	1·5122	1·3367	1·3368
0·5893	1·5056	1·5054	1·3346	1·3349
0·6868	1·4988	1·4986	1·3328	1·3328

Some interesting facts come out of a study of the dispersion formulæ. Just as for calcite and aragonite, the first ultra-violet frequency at 2000 A.U. in the case of the two nitrates also shows a marked anisotropy, its strength being almost completely confined to the plane of the NO_3 ion. This line is perpendicular to the optic axis in the calcite-like sodium nitrate and to the pseudo-hexagonal 'c' axis in potassium nitrate, which has the same structure as aragonite. On account of the large polarisation, it is reasonable to suppose that this electronic transition has its origin solely in the NO_3 ion. Then, one would expect that its strength in the plane would be the same for both $NaNO_3$ and KNO_3, since the nitrate ion is the same in both. This is indeed so as can be seen from Table I, if one allows for the differences in density between the two crystals and the consequent differences in the number of NO_3 ions per c.c. The ratio $a_\omega(2000) : a_2(2000)$ is 1·31. Now, the densities of $NaNO_3$ and KNO_3 are 2·267 and 2·113 respectively and dividing by their molecular weights, the ratio of the number of molecules per c.c. comes out to be 1·29, in close agreement with the above ratio for the strengths of the first ultra-violet frequency in the two cases.

In view of these successes of the theory, the author has ventured to calculate the refractive indices of $NaNO_3$ for wavelengths in the ultra-violet also from the dispersion formulæ given in Table I. They are shown in Table IV and would probably be found to be correct to 2 or 3 units in the third decimal place.

3. Thermal Variation of the Refractive Indices

The author has not been able to discover any references to measurements of dn/dt for sodium and potassium nitrates. Consequently, it is not possible to verify in these cases the thermo-optic theory developed in B1 for birefringent crystals. However, one may attempt to calculate dn/dt from theory for $NaNO_3$ on the analogy of calcite. As will be seen below, these calculations are rough and must be regarded as tentative.

Differentiating (1) and assuming that the extreme ultra-violet frequency does not alter with temperature, one gets

$$\left.\begin{aligned} 2n_\omega \frac{dn_\omega}{dt} &= -\gamma (n_\omega^2 - 1) \\ &+ \frac{2a_{1\omega}\lambda^4}{(\lambda^2 - 0{\cdot}121)^2} \cdot \chi_1 + \frac{2a_{2\omega}\lambda^4}{(\lambda^2 - 0{\cdot}4)^2} \cdot \chi_2 - \tfrac{1}{2}(\alpha_{\parallel} - \alpha_{\perp}) \cdot \frac{K\lambda^2}{\lambda^2 - 0{\cdot}4}, \\ 2n_e \frac{dn_e}{dt} &= -\gamma (n_e^2 - 1) \\ &+ \frac{2a_{1e}\lambda^4}{(\lambda^2 - 0{\cdot}121)^2} \cdot \chi_1 + \frac{2a_{2e}\lambda^4}{(\lambda^2 - 0{\cdot}4)^2} \cdot \chi_2 + (\alpha_{\parallel} - \alpha_{\perp}) \cdot \frac{K\lambda^2}{\lambda^2 - 0{\cdot}4}, \end{aligned}\right\} \quad (2)$$

using the same symbology as in B1. As for calcite, the variation due to the infra-red frequency is negligible, and the transfer in oscillator strength is taken to be sensible only for the nearest ultra-violet frequency at $0{\cdot}2\mu$. $\alpha_{\parallel}$ and $\alpha_{\perp}$ have the values 101×10^{-6} and $11{\cdot}5 \times 10^{-6}$ respectively at 50° C. (Saini and Mercier, 1934). The only quantities to be known are χ_1, χ_2 and K. We may obtain reasonable values for these from the following considerations. The Raman frequencies of $NaNO_3$ have been studied by Nedungadi (1938). The values of the frequencies ν as well as their temperature-variation $\chi = -(1/\nu)(d\nu/dt)$ may be compared with those of calcite as shown in Table III.

Table III

	Calcite				Sodium nitrate	
	ν in cm.$^{-1}$ at 25°	$\chi \times 10^{-6}$			ν in cm.$^{-1}$ at 25°	$\chi \times 10^{-6}$ Nedungadi
		V*	OW*	K*		
ν_4 ..	156	414	195	183	98	809
ν_5 ..	282	273	138	87	185	592
ν_2 ..	714	0	0	18	720	16
ν_0 ..	1087	0	0	0	1065	14
ν_3 ..	1432	..	..	8	1385	~10
$2\nu_1$ ..	1749	..	..	0	1667	..

* V = Venkateswarulu (1942); OW = Ornstein and Went (1935); K = Kopcewicz (1937).

As pointed out in B1, the measurements for calcite are very discrepant. However, it will be seen that the internal vibrations of the CO_3 and NO_3 ions show a great similarity. It is obvious that χ_2 must correspond to χ of the internal vibrations. In calcite, this had a value of about 30×10^{-6}, somewhat larger than χ of the internal Raman lines, which must be due to an interaction with the lattice vibration. In $NaNO_3$, not only is the electronic frequency lower (2000 A.U. as compared with 1535 A.U. in calcite), but the lattice vibrations also have much larger χ's. Hence, it would be reasonable to take $\chi_2 = 50 \times 10^{-6}$ in this case. As regards χ_1, this had a low value of 10×10^{-6} for calcite. In $NaNO_3$, one would expect it to be larger for the following reason. The binding in $NaNO_3$ is only due to a single valence electron while in $CaCO_3$, it is due to two electrons, so that the binding should be weaker. In fact, one might look for an analogy for this frequency to NaCl, in which the NO_3^- is replaced by Cl^-. For NaCl, the dispersion frequency with wavelength near about 1100 A.U. has a χ of the order of 30×10^{-6} (see A5). We therefore take χ_1 to have the same value, 30×10^{-6}. For K, we might take it to have the value 1·0, the same as for calcite. This, however, does not mean that the transfer is of the same magnitude as in calcite. In fact, it is much larger, on account of the larger thermal expansion of $NaNO_3$. We only assume that it is related to the expansion in the same way in both cases. With these assumptions, dn_ω/dt and dn_ϵ/dt have been calculated for a few wavelengths from Eqs. (2) and are given in Table IV. It will be useful to give here some idea of the relative magnitudes of the variations in refractive index due to change in volume, change in frequency and transfer of oscillator strength. At 5893 A.U. these three contributions to $2n\ dn/dt$ are respectively $-187{\cdot}4$, $+43{\cdot}6$ and $-50{\cdot}6 \times 10^{-6}$ for the ordinary ray, and $-97{\cdot}3$, $+9{\cdot}9$ and $+101{\cdot}2 \times 10^{-6}$ for the extraordinary ray. At 2537 A.U., the corresponding values are $-283{\cdot}4$, $+174{\cdot}9$, $-118{\cdot}4$; $-105{\cdot}4$, $+14{\cdot}2$, $+236{\cdot}8 \times 10^{-6}$. It will be seen that the third term due to transfer of oscillator strength is fairly important in this case. It may be mentioned again that the calculations are only tentative, being based on the assumptions made above. It will be interesting to see how far they fit the facts.

TABLE IV

λ in microns	n		λ in microns	$dn/dt \times 10^5$	
	Ordy.	Extrdy.		Ordy.	Extrdy.
0·3650	1·6391	1·3443	0·589	−5·9	+0·5
0·3131	1·6798	1·3494	0·436	−6·0	+0·9
0·2652	1·7695	1·3573	0·365	−6·0	+1·5
0·2536	1·8126	1·3602	0·254	−6·0	+5·3

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for the kind interest that he took in the investigation.

4. Summary

Dispersion formulæ have been developed for sodium and potassium nitrates on the basis of the theory developed in Part I of this series to explain the birefringence of crystals. Two dispersion frequencies at 2000 and 1100 A.U. and a constant term to represent a remote ultra-violet frequency suffice for both the indices of $NaNO_3$ and for KNO_3. The interesting result emerges that the nearest frequency at 2000 A.U. is practically inactive in a direction at right angles to the NO_3 ion, which fact is responsible for a major portion of the birefringence. Tentative calculations of the temperature-variation of the refractive indices have also been made for $NaNO_3$ which however could not be tested owing to the lack of experimental data.

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RAMAN SPECTRA OF METHYL ALCOHOL, ETHYL ALCOHOL AND *n*-HEPTANE

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1. Introduction

Organic compounds, especially those which are liquids at ordinary temperatures, have been favourite subjects for Raman Effect studies. Many such substances have been investigated and conclusions of a general nature have been reached regarding the characteristic frequencies of specific types of bonds and also regarding the relation of the spectra to molecular structure. A complete theoretical interpretation of the observed features of the spectra should be possible at least in some of the simpler cases, and this lends interest to such cases being examined experimentally with special care, using the most powerful technique available for exciting and recording the spectra.

In the great majority of investigations the λ 4047 and λ 4358 radiations of the mercury arc have been employed for obtaining the spectra. Although Rasetti, as early as 1929, developed the technique of using the λ 2537 radiation as exciter, only a few workers have utilised this technique, among whom may be mentioned specially Bolla (1934), Halford and others (1937); Spedding and Stamm (1942); Krishnan (1945). Compared with the other radiations of the arc, the intensity of the λ 2537 line is exceptionally great and so also is its scattering power in view of the λ^{-4} law. Moreover, the exciting radiation can be effectively suppressed from the scattered light by absorption in a column of mercury vapour before its entry into the spectrograph, thereby eliminating the general fogging of the plate by parasitic illumination. This enables very faint Raman lines and especially those with rather small frequency shifts to be successfully recorded and measured. The so-called 'wing' accompanying the Rayleigh line exhibited by liquids can also be satisfactorily recorded. The applicability of this technique is necessarily confined to substances which are transparent to the ultra-violet and which do not luminesce or get affected photochemically. This limitation no doubt precludes the aromatic organic compounds from the field of study; but this still leaves us with numerous compounds of the aliphatic

class which are transparent to the ultraviolet and therefore capable of investigation by this method, *e.g.*, hydrocarbons, alcohols, etc. In the present paper, the results obtained from a study of methyl alcohol, ethyl alcohol and *n*-heptane are described.

2. Earlier Work

Methyl alcohol has been one of the earliest liquids to be studied in Raman Effect and also one of the most frequently examined. Venkateswaran and Karl (1928) recorded only the four strong lines at 1031, 1462, 2832 and 2938 cm.$^{-1}$ An additional line at 1266 cm.$^{-1}$ was reported by Ganesan and Venkateswaran (1929) which, however, was not confirmed by Bhagavantam and Venkateswaran (1930) who reported two other Raman shifts at 286 and 777 cm.$^{-1}$ A faint band at 1362 cm.$^{-1}$ was first observed by Dadieu and Kohlrausch (1930) and another line at 1107 cm.$^{-1}$ by Wood and Collins (1932). The maximum number of Raman lines have been reported by Voge (1934), Mizushima and others (1936) which include lines at 1165, 2911 and 2980 cm.$^{-1}$ Edsall (1937) was the first to observe a faint band at 2589 cm.$^{-1}$ Halford, Kissin and Anderson (1937) studied the Raman spectrum of methanol using both λ 2537 and λ 4358 radiations as exciters. They, however, found no appreciable difference in the Raman shifts observed. The observations of all these workers are listed in Table I along with those of the present author.

Polarisation studies of the Raman lines in methyl alcohol have been made by Venkateswaran (1933), Trumpy (1934) and others. The infra-red absorption spectrum of the liquid and vapour have been exhaustively studied by Borden and Barker (1938) and Noether (1942). An assignment of the observed Raman frequencies to the oscillations inside the methyl alcohol molecule has been made by Halford and others based on these studies. Besides, Methanol has also been the subject of study by various authors in connection with the applications of Raman Spectra to problems like the formation of intermediate chemical compounds (Hibben, 1930; Sack and Brodskii, 1935, etc.); the study of the OH bond (Medard, 1934), etc.

Like methanol, ethyl alcohol has also been frequently studied mostly in the investigations on the Raman spectra of the homologous series of alcohols. Ganesan and Venkateswaran (1929), Daure (1929), Dadieu and Kohlrausch (1930), Sircar (1930) and others who were among the earlier investigators have reported only nine prominent Raman shifts occurring at about 430, 880, 1050, 1098, 1276, 1460, 2870, 2930 and 2980 cm.$^{-1}$ Nisi (1930) observed additional lines at 936 and 987 cm.$^{-1}$ A total of sixteen Raman lines was reported by Wood and Collins (1932) which included new

lines at 443, 1115, 1162, 1481, 2637 and 2714 cm.$^{-1}$ Holubei and Cauchois (1931) were probably the first to study the Raman spectrum under ultraviolet excitation. But their studies were not as successful as that of Bolla (1934) who undertook one of the most exhaustive studies of ethyl alcohol using the λ 2537 radiation as exciter. He observed about fifty-six Raman lines, forty-two of which were combinations of the fourteen fundamentals. Polarisation studies of the Raman lines have been made by Simons (1932), Trumpy and others. Numerous miscellaneous investigations pertaining to the applications of Raman spectra to the study of chemical reactions have also been made on ethyl alcohol by Hibben (1932), Parthasarathi (1934) and Goubeau (1933), etc.

Bonino and Brull (1929) who were the first to study the Raman spectrum of *n*-heptane could observe only nine Raman lines but Ganesan and Venkateswaran (1932) reported the existence of as many as twenty-eight Raman lines, most of which were confirmed by Sircar (1932) and Collins (1932) who investigated the low frequency shifts of *n*-heptane in connection with his study of a series of octanols and by Kohlrausch and Koppl (1934). It may be pointed out that all these investigations were carried out using the λ 4358 radiation for excitation of the Raman lines. The λ 2537 radiation has been used probably for the first time by the present author for the study of the Raman spectrum of *n*-heptane and the results obtained are tabulated in Table III.

3. Experimental

Technique.—The source of illumination employed in this investigation was a specially designed vertical quartz mercury arc, with a tungsten anode and mercury cathode. The arc was kept continuously evacuated by an efficient pump and the cathode end was kept immersed in running water. The discharge was pressed against the front wall of the tube by keeping the vertical portion of the arc between the pole-pieces of a powerful electromagnet. Under these conditions, there was no appreciable reversal of the 2537 line and the arc was found to be at its maximum intensity.

Raman Tube.—A specially made silica Wood's tube was used, one end of the tube being closed by fusing a silica disc to it and the other end drawn into a horn as usual. The horn-shaped end was joined to the side tube of a round-bottomed pyrex flask by a graded seal in such a manner that the Raman tube could be kept vertically by suitably clamping the flask. By this arrangement, the liquid could be directly distilled into the Raman tube from the flask in vacuum after evacuating and sealing the system.

Liquids.—The methyl alcohol used in the present investigation was Merck's acetone-free sample. The liquid was distilled ordinarily twice and finally distilled in vacuum into the Raman tube. Purity tests were made by measuring the refractive index and the specific gravity of the liquid. It was found to be 99·9% pure. Kahlbaum's ethyl alcohol and *n*-heptane were the other two liquids used. Both were distilled *in vacuo* finally after ordinary double distillation. Ethyl alcohol was found to be absolutely pure for our purpose according to the purity tests. *n*-Heptane was found to contain some of the higher homologues in traces, as its original source was petroleum, according to Kahlbaum. Therefore, necessary care was taken to reject the lines of its homologues which might also come up in the Raman spectrum observed.

Experimental Arrangement.—The Raman tube was kept vertical and parallel to the length of the arc so as to get the maximum column illuminated. The liquid was vigorously cooled by a fan. The flattened bottom end of the tube was covered fully with black paper except for a small aperture in the middle through which the scattered radiation was led into the slit of the spectrograph by reflection from a well aluminised mirror kept inside a specially made 45° adaptor. All essential precautions were taken to prevent stray illumination from entering the spectrograph.

The spectrograph used was a Hilger E_3 quartz instrument having a dispersion of about 140 $cm.^{-1}/mm.$ in the λ 2537 region. Exposures varying from a few hours to 48 hours were given to photograph the spectra, with slit widths of about 0·05 mm. Ilford special Rapid plates were usually used, and for comparison purposes, an iron arc spectrum of moderate intensity was usually superposed on the Raman spectra photographed. The negatives were measured under a Hilger cross-slide micrometer. Exceedingly faint lines were estimated visually from the iron-arc spectrum and verified from the microphotographs of the negative taken with a Moll microphotometer.

4. Results

The frequency shifts observed in methyl alcohol, ethyl alcohol and *n*-heptane with their visually estimated intensities (figures given in brackets) are given along with the results obtained by earlier workers in Tables I, II and III respectively. The most intense of the spectrograms obtained in each case are reproduced in Figs. 1, 3 and 4 as also the microphotometric records of lighter exposed plates. A description of these plates is given at the end.

TABLE I

Frequency shifts observed in Methyl Alcohol in wave numbers

Author	Edsall	Wood and Collins	Halford, Kissin and Anderson	Dadieu and Kohlrausch	Mizushima, Morino and Okamato	Venkateswaran and Bhagavantam
Bands extending upto						
Wing { 67						286 (0b)
Wing { 146						
Wing { 234						
491 (1)						777 (0b)
872 (3)						
922 (3)						
1032 (5)	1032 (6)	1028 (10)	1029 (6)	1035 (4)	1033 (6)	1034 (5)
1109 (4)	1114 (1)	1107 (2)	1104 (2)		1107 (2)	
1150 (3)	1163 (1)		1153 (1)		1165 (1)	
1370 (2b)			1370 ?			1365 (0)
1449 } (8)	1461 (5v.b)	1457 (1b)	1464 (5)	1454 (3 sbr)	1464 (5b)	1469 (5b)
1470 }						
2585 (2b)	2589 (1v.b)		2588 (1)			
	2839 (7b)	2729 (1)				
			2835 (10)	2832 (8)	2835 (10)	2835 (8)
2833 (10)		2831 (10)	2913 (4)		2911 (1)	
2911 (5)	2945 (6)		2936 (8)	2941 (7)	2940 (9)	2945 (6)
					2993 (3)	
2944 (9)		2942 (10)	2992 (4)			
2989 (5)						
3380 centre	3390 ± 200		3382 ± 100	3388 band	3270–3480b	Band

TABLE II

Frequency shifts observed in Ethyl Alcohol in wave numbers

Author	Venkateswaran and Ganesan	Dadieu and Kohlrausch	Nisi	Wood and Collins
Wing upto 168 cm.$^{-1}$				
254 (1)				
356) 382) (1)b				
427 (5)				426 (5)
436 (5)	450 (0)	431 (1)	437	443 (2)
529 (2)				
549 (2)				
777 (4)				
818 (4)				
886 (10)b	884 (5)	880 (5)	882	883 (2)
932 (4)			936	
1032 (4)	1047 (2)	1050 (3)	987	
1053 (10)		1098 (1)	1049	1047 (10)
			1104	1091 (1)
1095 (8)	1165 (2)			1115 (1)
1125 (1)				1162 (8)
1268 (1)	1272 (2)	1276 (1)	1274	1273 (10)
1457 (9)b				
1487 (7)b	1461 (3)	1457 (7b)	1454	1449 (10)
				1481 (4)
1622 (0)				
2082 (0)				
2471 (1)				
2530 (1)				
2587 (1)				2637 (0)
2717 (8)b				2714 (1)
2755 (5)				2823 (2)
2834 (8)b	2872 (2)	2873 (5b)	2878	2883 (10)
2881 (10)v. b.				2925 (10)
2931 (10)	2930 (3)	2926 (8b)	2927	2972 (10)
2978 (10)b	2973 (5)	2974 (5)	2975	
3236 (3 s.f.)		Band		Band
3400 Band (2)				

TABLE III

Frequency shifts observed in n-heptane in wave numbers

Author	Bonino and Brull	Sirkar	Kohlrausch and Koppl	Ganesan anfl Venkateswaran
				147 (1)
Wing apto 78 cm.$^{-1}$	154 (1)			274 (0)
313 (2)		304 (2)	309 (3)	312 (1)
398 (2)		398 (2b)	394 (2b)	346 (1)
445 (4)		441 (2)		407 (1)
			490 (0)	447 (1)
540 (2)		541 (2)		499 (0)
772 (8)	765 (2)	769 (4)	736 (0)	546 (1)
	822 (2)		774 (1b)	720 (0)
845 (5)		843 (2)	836 (3)	769 (3)
888 (5)	897 (1)	900 (2b)	900 (4)	845 (2)
901 (4)				
972 (8)	956 (1)	962 (3b)	938 (0)	903 (2)
1035 (5)	1027 (1)	1031 (2)	1013 (1)	967 (2)
1064 (4)				
1087 (5)				
1143 (8)		1080 (2b)	1046 (2)	1034 (3)
		1135 (1b)	1073 (3b)	1088 (1)
1166 (4)		1161 (2)	1134 (2b)	1132 (0)
		1242 (1b)	1160 (0)	1162 (1)
1206 (4)		1263 (2b)	1301 (6b)	1244 (1)
1253 (4)		1301 (3)	1359 (0)	1266 (1)
1268 (5)		1338 (1)	1439 (5)	1304 (2)
1301 (5)		1450 (5b)	1459 (6)	1348 (2)
1349 (4)				1400 (1)
				1453 (3)
1367 (2)				
1442 (10)	1448 (3)			
1460 (10)				
1654 (1)				
2523 (1)				
2610 (1)		2651 (1)		
			2720 (3sb)	
2657 (1)		2704 (2)		
2733 (2b)			2853 (12)	
2755 (10)		2854 (8b)	2874 (12)	2853 (4)
2875 (5)	2865 (5)			
			2902 (12)	2872 (3)
2877 (8)		2922 (6b)	2933	2912 (3)
2920 (8)				
2939 (10)	2932 (5)	2958 (4b)	2962	2931 (4)
2964 (8)				2963 (3)

5. Discussion of Results

Methyl Alcohol.—The most important feature brought out by the present investigation is the existence of a 'wing' accompanying the λ 2537 line with very great intensity on both sides of the exciting line. With a fast instrument like the Intermediate quartz spectrograph, the 'wing' could be observed after an exposure of only 4 hours. Fig. 1(*b*) shows how far the wing extends and how intense it is. Although numerous workers have studied the Raman spectrum of this liquid under different methods of excitation, the occurrence of a 'wing' of this type has not been reported in literature. In fact, methyl alcohol has been used to dilute benzene in the study of the 'wing' exhibited by benzene (Sirkar, 1932). The possibility that the appearance of the 'wing' may be due to the halation produced by the over-exposure of the λ 2537 radiation is ruled out, because, as pointed out earlier, it is the singular advantage in using this line for excitation that it can be effectively filtered from the scattered light, before its entry into the spectrograph by absorbing it over a column of mercury vapour. Thus the existence of the 'wing' is genuine and its presence in the spectrum of an aliphatic liquid like methyl alcohol has been shown clearly for the first time.

A more interesting fact about the wing is that it exhibits a definite structure (see Fig. 2). There is a distinct fall in the intensity of the wing at about 67 cm.$^{-1}$, followed by another intensity drop at about 147 cm.$^{-1}$ and finally, the wing fades out at about 234 cm.$^{-1}$ These three clearly discernible parts observed, naturally suggest that the origin of the wing may lie in the possible modes of rotation of the CH_3OH molecule. However, more detailed investigations, specially taking into account the associating nature of the liquid are in progress to elicit more information on this new feature in the spectrum.

Besides the observation of this 'wing', the entire Raman spectrum of methyl alcohol has been photographed. It will be found from Table I that the observed frequency shifts include the important lines, observed by all previous workers, like the C–H frequencies at about 2800 cm.$^{-1}$, the C–O vibration at about 1030 cm.$^{-1}$ Although previous workers were not able to observe the 1460 cm.$^{-1}$ band well resolved, two intensity maxima at 1449 and 1470 cm.$^{-1}$ were discernible. The O–H band at about 3400 has also been observed clearly, as also the faint bands at 1370 and 2590 cm.$^{-1}$

Three new Raman lines at 492, 876 and 922 cm.$^{-1}$ have also been observed by the present author and these appear on all moderately exposed spectrograms. The 876 and 922 lines are appreciably intense and sharp. The possibility that these lines may owe their origin to excitation

by other radiations of the arc has also been examined and found unlikely. No line corresponding to 1266 cm.$^{-1}$ was observed by the author and it is quite likely that this line which has been reported by some previous workers may be the 1040 line excited by the 4047 radiation, as pointed out by Hibben (1932).

Ethyl Alcohol.—Six new Raman lines were observed in ethyl alcohol in the region below 1000 cm.$^{-1}$ These have not been reported by Bolla, who found many lines in the region above 3000 cm.$^{-1}$, none of which have been confirmed by the present author excepting the O–H band at 3400 cm.$^{-1}$ and the line at 3236 cm.$^{-1}$ It is not likely that the faint lines observed by the present author at 2052 cm.$^{-1}$ and 2530 cm.$^{-1}$ are really the low frequency shifts at about 360 and 815 excited by the λ 2652 line of the arc. There is a wing in the spectrum of ethyl alcohol also accompanying the Rayleigh line, although it is not so prominent as the one observed in methyl alcohol and does not possess any structure. The 'wing' extends upto nearly 168 wave numbers. All the 14 fundamental frequencies observed by Bolla are found to exist; but the existence of many of their combinations reported by him is highly doubtful.

n-*Heptane.*—An exposure of about one hour was sufficient to bring out the prominent lines in the Raman spectrum of *n*-heptane. In about sixteen hours the complete spectrum was photographed, which showed thirty-three Raman lines. As purity tests indicated that a very small amount of higher hydrocarbons might be present in the liquid, a search was made on the observed Raman lines to see whether any of them could be attributed to the impurities, especially octane, etc. None of the lines could be rejected on that score. The possibility that some of the fainter lines might in reality have been excited by other radiations of the arc was also examined thoroughly. The low frequency shifts at 147 and 207 cm.$^{-1}$ reported by some earlier authors have not been observed and are not considered likely to exist. An interesting photochemical change was observed in *n*-heptane after exposure to ultraviolet radiation. The liquid acquired a foul odour and a reddish brown deposit was found on the walls of the container, indicating possibly the occurrence of a kind of polymerisation under the action of λ 2537 radiation, similar to the mercury sensitised photochemical polymerisation of cyclopropane observed by Harris and others (1936).

In conclusion, the author desires to express his deep sense of gratitude to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his inspiring guidance and the keen interest evinced by him in this investigation. The author also wishes to thank Dr. R. S. Krishnan for his kind help in setting up the technique employed in this investigation.

6. Summary

The advantages of using the λ 2537 reasonance radiation of the mercury arc lamp are set forth and the technique of employing this radiation for the study of Raman spectra of liquids described. Results obtained from an investigation of the Raman spectra of methyl alcohol, ethyl alcohol and *n*-heptane are given along with a brief review of the earlier work done on these liquids. The existence of a wing of considerable intensity accompanying the Rayleigh line in the Raman spectrum of methyl alcohol has been observed. Three distinct bands are observed in the wing, which extends upto 234 cm.$^{-1}$ The wing has also been shown to be present in the Raman spectrum of ethyl alcohol, extending upto 150 cm.$^{-1}$, and to a considerably less extent in *n*-heptane also. New Raman frequencies have been observed in all these liquids. A fairly complete bibliography of the important work done on the Raman spectra of these liquids is also included.

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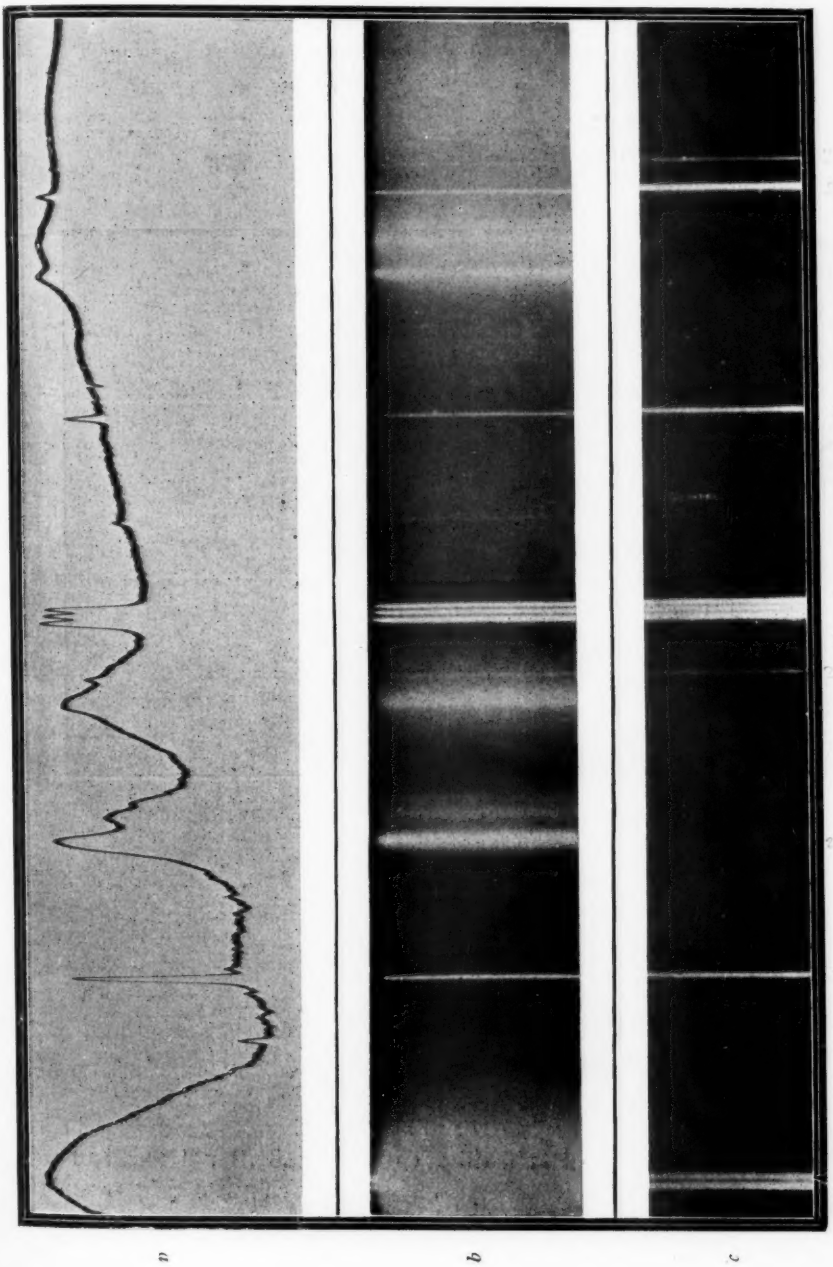

FIG. 1

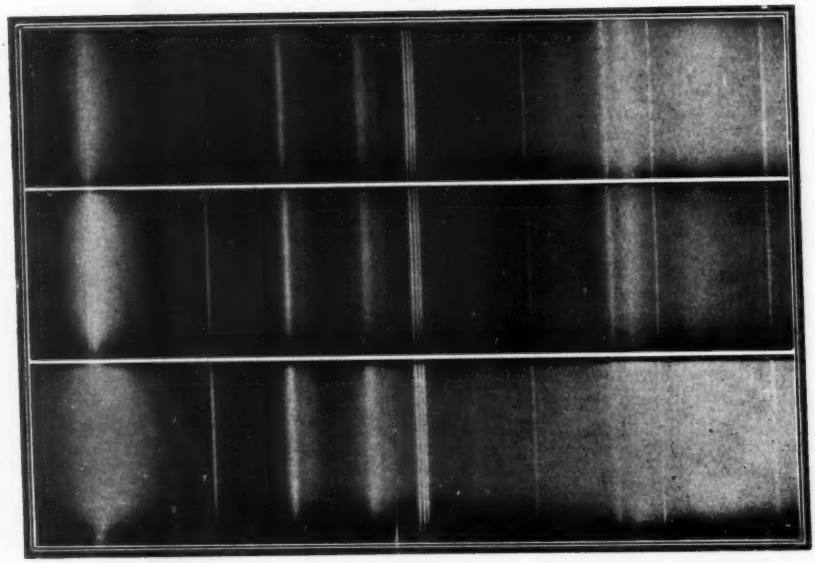

FIG. 2

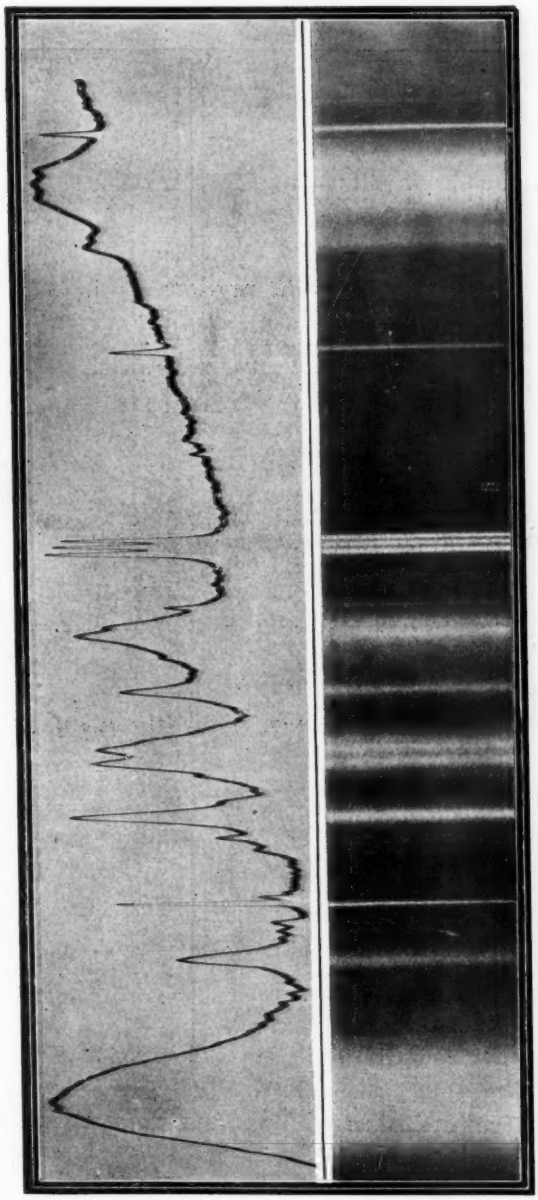

FIG. 3

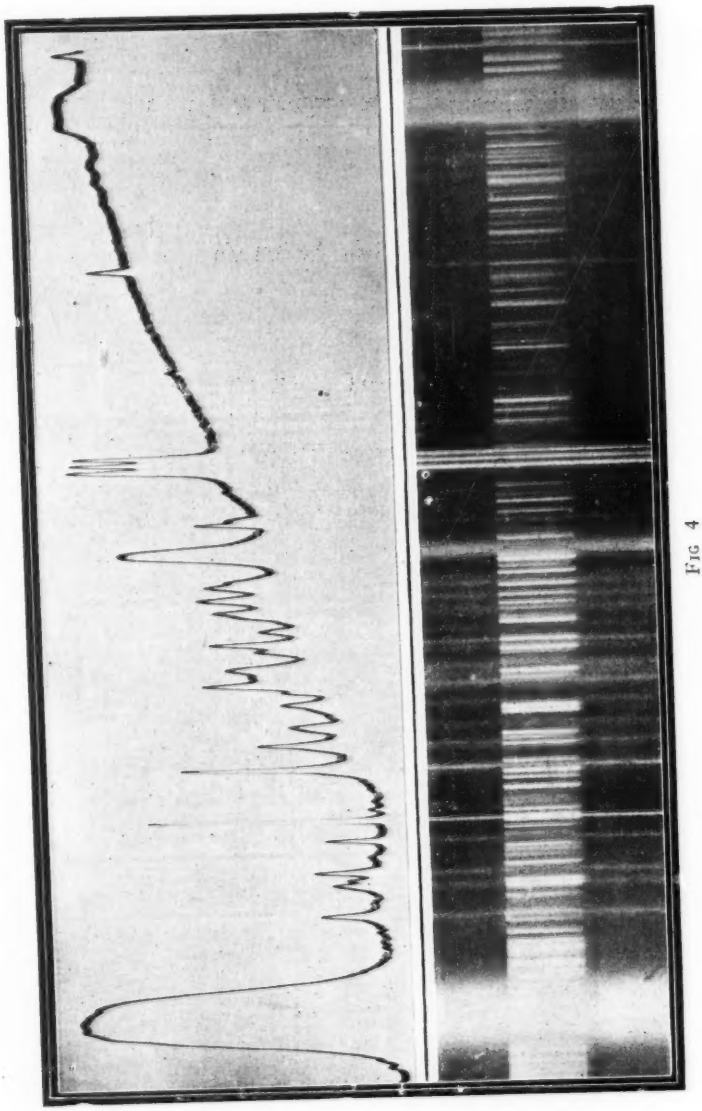

FIG 4

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Description of Plates

Fig. 1, *a*. Mercury spectrum taken with E_3 quartz spectrograph. The arrow indicates the exciting line λ 2536·5. From left to right in the spectrum, the prominent mercury lines observed are λ 2534, 2536·5, 2563·9, 2576·3, 2603·2, 2639·9, 2652·0, 2653·7, 2655·1, 2675·0, 2698·9, 2752·8, 2759·7 respectively.

b. Raman spectrum of methyl alcohol.

c. Its microphotometric record.

Fig. 2. (*a*, *b* and *c*) Raman spectrum of methyl alcohol, printed with varied exposures to show the structure of the 'wing'.

Fig. 3 *a*. Raman spectrum of ethyl alcohol.

b. Its microphotometric record.

Fig. 4 *a*. Raman spectrum of *n*-heptane.

b. Its microphotometric record.

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